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(54) UNDERWATER USE TYPE RARE EARTH-BASE PERMANENT MAGNET AND
METHOD FOR MANUFACTURING THE SAME

(57)Abstract:

PROBLEM TO BE SOLVED: To provide an underwater use type rare earth-base permanent magnet which exhibits excellent corrosion resistance even when used by being immersed in an oxidative electrolyte solution (etchant) having high corrosiveness, and a method for manufacturing the same.

SOLUTION: The permanent magnet is constituted by forming an Ni plating film having characteristics of ≥ -0.1 V in natural electrode potential (to an SCE saturated calomel electrode) in an aqueous solution containing 10 ppm Cu ions and ≥ 0 V in an aqueous solution containing 100 ppm Cu ions on the extreme surface layer of the magnet surface.

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CLAIMS

[Claim(s)]

[Claim 1] The subaqueous use mold rare earth system permanent magnet characterized by forming in the maximum surface on the front face of a magnet nickel plating coat which has a property beyond 0V in the water solution which is more than -0.1V in the water solution with which natural electrode potential (saturated calomel electrode for S C E) contains 10 ppm of Cu ion, and contains 100 ppm of Cu ion.

[Claim 2] The subaqueous use mold rare earth system permanent magnet according to claim 1 characterized by containing S to which said nickel plating coat makes an aromatic series sulfonic acid or its salt a source of supply.

[Claim 3] The subaqueous use mold rare earth system permanent magnet according to claim 2 characterized by S content of said nickel plating coat being 10 ppm - 800 ppm.

[Claim 4] The subaqueous use mold rare earth system permanent magnet according to claim 1 to 3 characterized by the diameter of average electrocrystallization crystal grain of said nickel plating coat being 0.1 micrometers or less.

[Claim 5] The subaqueous use mold rare earth system permanent magnet according to claim 1 to 4 characterized by the thickness of said nickel plating coat as the maximum surface for forming a composite-plating coat layer in a magnet front face being 0.1 micrometers - 10 micrometers.

[Claim 6] The subaqueous use mold rare earth system permanent magnet according to claim 5 characterized by being formed in the front face of nickel plating coat with which said nickel plating coat serves as a lower layer.

[Claim 7] The subaqueous use mold rare earth system permanent magnet according to claim 1 to 6 characterized by a rare earth system permanent magnet being a R-Fe-B system permanent magnet.

[Claim 8] The manufacture approach of the subaqueous-use mold rare-earth system permanent magnet characterize by to form in the maximum surface on the front face of a magnet nickel plating coat which have a property beyond 0V in the water solution which be more than -0.1V in the water solution with which natural electrode potential (saturated calomel electrode for S C E) contain 10 ppm of Cu ion by perform electric nickel plating using nickel plating liquid containing an aromatic series sulfonic acid or its salt , and contain 100 ppm of Cu ion .

[Claim 9] Operation for manufacturing the aromatic series sulfonic acid characterized by making an aromatic series sulfonic acid or its salt contain in nickel plating liquid, or the rare earth system permanent magnet of the salt so that the natural electrode potential in the water solution of nickel plating coat formed in the maximum surface of a rare earth system permanent magnet front face may turn into Cu ion and more than the reversible electrode potential (Cu²⁺/Cu reversible electrode potential) of Cu.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the subaqueous use mold rare earth system permanent magnet which demonstrates the corrosion resistance which was excellent even if it immersed and used it for the corrosive high electrolytic solution (etching fluid) by the oxidizing quality, and its manufacture approach.

[0002]

[Description of the Prior Art] Although rare earth system permanent magnets, such as a R-Fe-B system permanent magnet represented by the Nd-Fe-B system permanent magnet, have high magnetic properties, since the metal kind (especially R) which oxidation corrosion is easy to be carried out is included, when it is used without performing surface treatment, under the effect of a slight acid and alkali, moisture, etc., corrosion will advance from a front face, rust will be generated, and they will cause degradation and dispersion of magnetic properties in connection with it. Furthermore, when rust is generated to the magnet built into equipments, such as a magnetic circuit, there is a possibility of rust dispersing and polluting circumference components. Therefore, in order to avoid these troubles, forming nickel plating coat as a corrosion-resistant coat in the front face is performed by electric nickel plating that the corrosion resistance required of this magnet should be given from the former.

[0003]

[Problem(s) to be Solved by the Invention] By the way, although the ferrite magnet excellent in corrosion resistance has been used from the former as a magnet used for the motor for the submersible pump the object for well drawing-water raising, and for liquid sending, a household-electric-appliances liquid-sending pump, and the heat exchanger components of an automobile etc., using it from the request of space-saving-izing by the miniaturization of a pump, a motor, etc., energy saving by effectiveness rise, etc., replacing with a ferrite magnet the rare earth system permanent magnet which has high magnetic properties is examined. However, in order to present with a rare earth system permanent magnet these applications used underwater, the corrosion resistance superior to what is used in atmospheric air with a natural thing is required. The environment where a magnet is used may turn into a corrosive high electrolytic solution (etching fluid) environment by the oxidizing quality especially under the effect of impurity ion, such as Cu ion mixed unescapable from the component of the liquid circulatory system, atmospheric environment, supply liquid, etc. in the motor for heat exchanger components, such as air-conditioner evaporators, such as household electric appliances and an automobile, a capacitor, a radiator, and a heating heater, a chlorine ion (salinity), sulfate ion, nitrate ion, and carbonate ion, dissolved oxygen, etc. Since corrosive is high as for Cu ion or a chlorine ion, it divides also in impurity ion and Cu ion is a strong oxidizing quality, Even when nickel plating coat is formed in a rare earth system permanent magnet front face, Cu ion carries out a permutation deposit on nickel plating coat front face. The origin of corrosion comes or The inclination to form a local battery and to advance corrosion of the depth direction is strong, and there is a problem on use of magnetic properties deteriorating greatly as a result by corrosion (pitting and pitting) which results in a magnet base. Therefore, in using a rare earth system permanent magnet underwater, it becomes an important technical problem how corrosion resistance is raised to Cu ion or a chlorine ion. Then, this invention

aims at offering the subaqueous use mold rare earth system permanent magnet which demonstrates the corrosion resistance which was excellent even if it immersed and used it for the corrosive high electrolytic solution (etching fluid) by the oxidizing quality, and its manufacture approach.

[0004]

[Means for Solving the Problem] Set this invention persons in the process in which various examination is performed in view of the above-mentioned point, and they pay their attention to Cu ion in a water solution, and the reversible electrode potential (Cu^{2+}/Cu reversible electrode potential) of Cu. When natural electrode potential formed in the maximum surface of a rare earth system permanent magnet front face nickel plating coat which has the property more than of this reversible electrode potential, the knowledge of the magnet which demonstrates the corrosion resistance which was excellent even if it immersed and used it for the corrosive high electrolytic solution (etching fluid) by the oxidizing quality being obtained was carried out.

[0005] This invention is made based on the above-mentioned knowledge, and the subaqueous use mold rare earth system permanent magnet of this invention is characterized by forming in the maximum surface on the front face of a magnet nickel plating coat which has a property beyond 0V in the water solution which is more than -0.1V in the water solution with which natural electrode potential (saturated calomel electrode for S C E) contains 10 ppm of Cu ion, and contains 100 ppm of Cu ion a passage according to claim 1. Moreover, a subaqueous use mold rare earth system permanent magnet according to claim 2 is characterized by containing S to which said nickel plating coat makes an aromatic series sulfonic acid or its salt a source of supply in a subaqueous use mold rare earth system permanent magnet according to claim 1. Moreover, a subaqueous use mold rare earth system permanent magnet according to claim 3 is characterized by S content of said nickel plating coat being 10 ppm - 800 ppm in a subaqueous use mold rare earth system permanent magnet according to claim 2. Moreover, a subaqueous use mold rare earth system permanent magnet according to claim 4 is characterized by the diameter of average electrocrystallization crystal grain of said nickel plating coat being 0.1 micrometers or less in a subaqueous use mold rare earth system permanent magnet according to claim 1 to 3. Moreover, a subaqueous use mold rare earth system permanent magnet according to claim 5 is characterized by the thickness of said nickel plating coat as the maximum surface for forming a composite-plating coat layer in a magnet front face being 0.1 micrometers - 10 micrometers in a subaqueous use mold rare earth system permanent magnet according to claim 1 to 4. Moreover, a subaqueous use mold rare earth system permanent magnet according to claim 6 is characterized by being formed in the front face of nickel plating coat with which said nickel plating coat serves as a lower layer in a subaqueous use mold rare earth system permanent magnet according to claim 5. Moreover, a subaqueous use mold rare earth system permanent magnet according to claim 7 is characterized by a rare earth system permanent magnet being a R-Fe-B system permanent magnet in a subaqueous use mold rare earth system permanent magnet according to claim 1 to 6. Moreover, the manufacture approach of the subaqueous use mold rare earth system permanent magnet of this invention By performing electric nickel plating a passage according to claim 8 using nickel plating liquid containing an aromatic series sulfonic acid or its salt It is characterized by preparing nickel plating coat which has a property beyond 0V in the water solution which is more than -0.1V in the water solution with which natural electrode potential (saturated calomel electrode for S C E) contains 10 ppm of Cu ion, and contains 100 ppm of Cu ion in the maximum surface on the front face of a magnet. Moreover, a passage according to claim 9, operation for manufacturing the aromatic series sulfonic acid of this invention or the rare earth system permanent magnet of the salt is characterized by making an aromatic series sulfonic acid or its salt contain in nickel plating liquid so that the natural electrode potential in the water solution of nickel plating coat formed in the maximum surface of a rare earth system permanent magnet front face may turn into Cu ion and more than the reversible electrode potential (Cu^{2+}/Cu reversible electrode potential) of Cu.

[0006]

[Embodiment of the Invention] The subaqueous use mold rare earth system permanent magnet of this invention is characterized by forming in the maximum surface on the front face of a magnet nickel plating coat which has a property beyond 0V in the water solution which is more than -0.1V in the water solution with which natural electrode potential (saturated calomel electrode for S C E)

contains 10 ppm of Cu ion, and contains 100 ppm of Cu ion. By forming in the maximum surface of a rare earth system permanent magnet front face nickel plating coat which has this property, it considers as the magnet which demonstrates the corrosion resistance which was excellent even if it immersed and used the natural electrode potential in the water solution of this coat for the corrosive high electrolytic solution (etching fluid) by the oxidizing quality by carrying out to more than the reversible electrode potential (Cu^{2+}/Cu reversible electrode potential) of Cu ion and Cu. In addition, it is desirable to form nickel plating coat which has a property beyond 0.1V in the water solution which is more than 0V in the water solution with which natural electrode potential (saturated calomel electrode for S C E) contains 10 ppm of Cu ion in order to give the more excellent corrosion resistance, and contains 100 ppm of Cu ion.

[0007] In this invention, natural electrode potential means the potential between nickel at the time of two or more chemical reactions having occurred on the front face of nickel plating coat into the water solution, and a water solution. Specifically The mixed potential based on the lytic reaction (nickel \rightarrow nickel $^{2+}+2e$) of nickel as an anode reaction, the reduction reaction ($\text{Cu}^{2+}+2e\rightarrow\text{Cu}$ and $\text{Cu}^{2+}+e\rightarrow\text{Cu}^+$) of Cu ion as a cathode reaction, the reduction reaction ($\text{O}_2+2\text{H}_2\text{O}+4e\rightarrow 4\text{OH}^-$) of dissolved oxygen, etc. is meant.

[0008] It is more than -0.1V in the water solution with which natural electrode potential (saturated calomel electrode for S C E) contains 10 ppm of Cu ion. and as an approach of forming in the maximum surface of a rare earth system permanent magnet front face nickel plating coat which has a property beyond 0V in the water solution containing 100 ppm of Cu ion For example, there is a method of making nickel plating coat contain S which makes an aromatic series sulfonic acid or its salt a source of supply by performing electric nickel plating using nickel plating liquid containing an aromatic series sulfonic acid or its salt.

[0009] electric nickel plating of a rare earth system permanent magnet -- setting -- a general plating bath (Watts bath etc.) presentation -- if independent, it is precise, and since nickel plating coat excellent in glossiness cannot be formed, the approach of making S which makes the aromatic series sulfone imide represented by saccharin in a plating coat and an aromatic series sulfonamide a source of supply contain from the former, and carrying out eburnation of the plating coat is adopted widely. However, if it does in this way and S is made to contain in a plating coat, since the surface potential of nickel plating coat will fall, own corrosion resistance of a plating coat will fall electrochemically. It faces forming a multilayer nickel plating coat in a rare earth system permanent magnet front face using the above-mentioned phenomenon. Make only nickel plating coat of the maximum surface contain S, or (see JP,2-23603,A) The content of S is made [many], so that it becomes the upper nickel plating coat from a magnet front face. Although the method of raising the corrosion resistance as the whole as the upper nickel plating coat is made to corrode preferentially in what surface potential is intentionally lowered for (see for example, JP,4-267305,A and the patent No. 2941446 official report) is proposed When such a magnet is used in the etching fluid containing Cu ion etc., Cu ion carries out a permutation deposit on nickel plating coat front face because the natural electrode potential of nickel plating coat of the maximum surface on the front face of a magnet becomes lower than Cu^{2+}/Cu reversible electrode potential. The result, Corrosion advanced and sufficient corrosion resistance was not able to be secured. However, by examination of this invention persons, although the above problems arise when aromatic series sulfone imide and the aromatic series sulfonamide which are made to contain in nickel plating coat and which are widely used as a source of supply of S are used When an aromatic series sulfonic acid or its salt was used as a source of supply of S, it became clear that nickel plating coat which demonstrates the corrosion resistance which was excellent even if it immersed and used it for the etching fluid containing Cu ion etc. was formed.

[0010] Here, as an aromatic series sulfonic acid, benzenesulfonic acid, 1, 3, 6 naphthalene tris RUHON acid, etc. are mentioned. Sodium salt, potassium salt, etc. are mentioned as a salt of an aromatic series sulfonic acid.

[0011] As for the aromatic series sulfonic acid to nickel plating liquid, or addition of the salt, it is desirable to carry out so that S content of nickel plating coat formed may be set to 10 ppm - 800 ppm. When there are few S contents of nickel plating coat formed than 10 ppm, there is a possibility that the effectiveness may not fully be demonstrated, and when [than 800 ppm] more, there is a

possibility of becoming nickel plating coat which is weak and lacks in adhesion.

[0012] the very thing which special limitation of the nickel plating liquid set as an aromatic series sulfonic acid or the addition object of the salt is not carried out, and is used for electric nickel plating -- it is easy to be used for a well-known thing, for example, a Watts bath, a sulfamic acid bath, a chloride bath, a way **** ghost bath, an ammonium-chloride bath, etc. the very thing according to the plating bath of each [conditions / electric / nickel plating] -- what is necessary is just to carry out by setting up well-known conditions In addition, it is [heat treatment / (baking)] good [in a line] at 150 degrees C - 250 degrees C in atmospheric air after electric nickel plating for 10 minutes to about 1 hour if needed. By this processing, the natural electrode potential in the inside of the water solution of nickel plating coat formed can be moved in the more **** direction.

[0013] As for nickel plating coat which has a property beyond 0V in the water solution which is more than -0.1V in the water solution with which natural electrode potential (saturated calomel electrode for S C E) contains 10 ppm of Cu ion, and contains 100 ppm of Cu ion, it is desirable to form so that the diameter of average electrocrystallization crystal grain may be set to 0.1 micrometers or less from a viewpoint of the eburnation of a coat. Such a plating coat can add the above-mentioned aromatic series sulfonic acid or its salt independently in nickel plating liquid, or can form this by adding combining alcoholic system additives, such as a polyethylene glycol, etc. In addition, the diameter of electrocrystallization crystal grain can be measured by observation by FE-SEM (field emission mold scan microscope) or AFM (atomic force microscope).

[0014] It is more than -0.1V in the water solution with which natural electrode potential (saturated calomel electrode for S C E) contains 10 ppm of Cu ion. And the thickness of nickel plating coat which has a property beyond 0V in the water solution containing 100 ppm of Cu ion When forming this nickel plating coat in the maximum surface for [when forming only this nickel plating coat in a rare earth system permanent magnet front face / 5 micrometers - 30 micrometers are desirable, and] forming a composite-plating coat layer in a magnet front face, 0.1 micrometers - 10 micrometers are desirable. That lower layer in the case of forming this nickel plating coat in the maximum surface for forming a composite-plating coat layer in a magnet front face Good with various metal plating coats including nickel plating coat formed by the well-known approach the very thing, such as wet plating, such as electroplating and nonelectrolytic plating, and a vapor plating, -- The 2nd layer (the maximum surface) with nickel plating coat with the 1st well-known layer For example, this nickel plating coat, The gestalt of this nickel plating coat etc. has the 3rd layer (the maximum surface) with Cu plating coat with the 2nd well-known layer [3rd] (the maximum surface) with this nickel plating coat and nickel plating coat with the 1st well-known layer layer with the 1st layer and nickel plating coat with the 2nd well-known layer.

[0015] The rare earth elements (R) in a R-Fe-B system permanent magnet have at least one sort or a still more desirable thing containing at least one sort in La, Ce, Gd, Er, Eu, Tm, Yb, Lu, and Y among Nd, Pr, Dy, Ho, Tb, and Sm among the rare earth system permanent magnets applied to this invention. Moreover, although it is usually sufficient with one sort in R, it can be practically used for any expedient reason of acquisition of two or more sorts of mixture (a misch metal, didym, etc.). Furthermore, it becomes possible by adding at least one sort in aluminum, Ti, V, Cr, Mn, Bi, Nb, Ta, Mo, W, Sb, germanium, Sn, Zr, nickel, Si, Zn, Hf, and Ga to attain improvement of the square shape nature of coercive force or a demagnetization curve, improvement of manufacturability, and low-pricing. Moreover, the temperature characteristic can be improved by permuting a part of Fe by Co, without spoiling the magnetic properties of the magnet obtained.

[0016]

[Example] Although the following examples explain this invention to a detail further, this invention is not limited to the following publications at all.

[0017] Aging treatment was performed at 600 degrees C among the argon ambient atmosphere for 2 hours, the sintered compact with the presentation of 15Nd-1Dy-7B-77Fe (atomic %) produced with powder-metallurgy processing was processed into plate-like [with the thickness of 2mm, a width of face / of 15mm /, and a die length of 30mm], and acid-washing defecation of the sintered magnet obtained by performing barrel beveling processing further was carried out with the dilution nitric acid. After rinsing, further, by lye, electrolytic cleaning was carried out and it rinsed. nickel plating liquid which adjusted pH for propargyl alcohol to 4 including 0.5 g/l as a nickel sulfate and 6 hydrate

260 g/l, a nickel chloride and 6 hydrate 40 g/l, boric-acid 40 g/l, and an additive was used to this magnet, and thickness formed in the magnet front face on electric nickel plating conditions of nickel plate by using as the 1st-layer plating coat nickel plating coat which is 20 micrometers as 50 degrees C of solution temperature of a plating bath, current density 0.2 A/dm², and an anode plate. Next, a nickel sulfate and 6 hydrate 300 g/l, a nickel chloride and 6 50g [l.] hydrate, The additive adjusted to various kinds of concentration shown in boric-acid 30 g/l, sodium-citrate 10 g/l, and Table 1 is included. nickel plating liquid which adjusted pH to 4 was used, and thickness formed in the 1st-layer plating coat front face on electric nickel plating conditions of nickel plate by using as the 2nd-layer (maximum surface) plating coat nickel plating coat which is 5 micrometers as 50 degrees C of solution temperature of a plating bath, current density 0.3 A/dm², and an anode plate. S content measured about the 2nd layer nickel plating coat using EPMA (electron probe microanalyzer: EPM [by Shimadzu Corp.]- 810 use) and the diameter of average electrocrystallization crystal grain measured using AFM (atomic force microscope: SPM[by Shimadzu Corp.]- 9500 use) are shown in Table 1. After rinsing the plating magnet sample obtained as mentioned above and making it dry, The etching fluid 1 which is 50 degrees C in which Cu ion 100ppm (it adjusts by a copper chloride and 2 hydrate) and 200 ppm (it adjusts with a sodium chloride) of chlorine ions are contained, and dissolved oxygen exists this further, While being immersed in the etching fluid 2 (pH is 6.5-7 for any etching fluid) which is 50 degrees C in which Cu ion 10ppm (**) and 200 ppm (**) of chlorine ions are contained, and dissolved oxygen exists further and measuring the natural electrode potential of a 2nd layer nickel plating coat, the engine performance was evaluated. A result is shown in Table 1. [0018] In Table 1, measurement of natural electrode potential was performed by [as being the following]. That is, etching fluid was put into 500ml beaker, and it considered as 50 degrees C of solution temperature. After the plating magnet sample was immersed in etching fluid, it carried out after 30-minute progress by measuring the potential on the front face of a sample with commercial potentiostat equipment using the glass Luggin capillary which carried out agar stuffing of the common saturation potassium chloride solution by using a reference electrode as the S C E saturated calomel electrode (as for measurement of natural electrode potential, it is desirable to carry out after etching fluid immersion 20 minutes - by which the potential of nickel plating coat front face is stabilized, and 30-minute progress). In addition, this measurement was performed, stirring the inside of a beaker by 500rpm with a magnet stirrer.

[0019] The compactness of a plating coat and corrosion-resistant promotion evaluation (coloring reaction trial) performed evaluation of the coat soundness in Table 1. It is as follows when the evaluation approach is explained briefly. The plating magnet sample was immersed in the test fluid adjusted to pH2 with potassium ferricyanide 3 g/l, ethanol 100 ml/l, and a hydrochloric acid in ordinary temperature, and it observed for 60 minutes. Since the blue spot occurred when corrosion resulted in a magnet material or coat defects (pinhole etc.) existed in it, when after 60-minute immersion did not have generating of a blue spot, a blue spot occurred in 30 minutes or more after O and immersion and a blue spot occurred in ** and 10 minutes - 20 minutes after immersion, it was estimated as x.

[0020] It carried out by the corrosion resistance evaluation in Table 1 being immersed in etching fluid 1 of 50 degrees C of solution temperature in a plating magnet sample for 1000 hours, investigating magnetic-properties degradation based on generating of rust and the amount measurement of flux after magnetization, and not having rust generating, and estimating it as O, when a demagnetizing factor is 1% or less, and estimating it as x, when other.

[0021]

[Table 1]

Niめっき液添加剤		添加量 (g/l)	S含量 (ppm)	平均電析 結晶粒径 (μm)	自然電極電位		被膜 健全性	耐食性	備考
					浸漬30分後のmV vs SCE				
					腐食液1 Cu ²⁺ :100ppm	腐食液2 Cu ²⁺ :10ppm			
1	1,3,6ナフトレントリスルホン酸ナトリウム	0.8	200	<0.1	+220	+180	○	○	本発明例
2	ベンゼンスルホン酸	1	250	<0.1	+150	+90	○	○	本発明例
3	1,3,6ナフトレントリスルホン酸ナトリウム +アリスルホン酸	2+0.5	300	<0.1	+220	+150	○	○	本発明例
4	1,3,6ナフトレントリスルホン酸ナトリウム +ポリエチレングリコール分子量1000	5+0.05	700	<0.1	+170	+120	○	○	本発明例
5	チオ尿素+プロパギルアルコール	1+0.5	≤20	<0.1	+230	+180	○	○	本発明例
6	ポリエチレングリコール分子量3000	0.03	≤20	<0.1	+180	+150	○	○	本発明例
7	サッカリン	5	800	<0.1	-50	-100	×	×	比較例
8	サッカリン+2ブチン1,4ジオール	3+0.5	500	<0.1	-10	-70	△	×	比較例
9	パトリスルホンアミド	10	1200	<0.1	-30	-150	×	×	比較例

[0022] By performing electric nickel plating using nickel plating liquid containing an aromatic series sulfonic acid or its salt so that clearly from Table 1 It is more than -0.1V in the water solution with which natural electrode potential (saturated calomel electrode for S C E) contains 10 ppm of Cu ion. And it turned out that it has a property beyond 0V in the water solution containing 100 ppm of Cu ion, and nickel plating coat which demonstrates the corrosion resistance which was excellent even if it immersed and used it for etching fluid can be formed. On the other hand, when electric nickel plating is performed using nickel plating liquid containing aromatic series sulfone imide or an aromatic series sulfonamide, nickel plating coat formed Even if comparable as S content of nickel plating coat formed by performing electric nickel plating using nickel plating liquid with which the S content contains an aromatic series sulfonic acid and its salt It turned out that the natural electrode potential in the inside of a water solution falls greatly, and serves as **, and corrosion resistance cannot be maintained when it is immersed and used for etching fluid. It is guessed that this difference is a thing based on the homogeneous difference of distribution of the difference in the deposit condition of these additives as a source of supply of S in the inside of nickel plating coat between the cases where the case where an aromatic series sulfonic acid and its salt are used as a source of supply of S, aromatic series sulfone imide, and an aromatic series sulfonamide are used as a source of supply of S formed, and S in nickel plating coat. Moreover, also when the case where it adds in nickel plating liquid combining thiourea and propargyl alcohol, and a polyethylene glycol were added in nickel plating liquid, it turned out that the same effectiveness as an aromatic series sulfonic acid or its salt is acquired.

[0023]

[Effect of the Invention] The subaqueous use mold rare earth system permanent magnet of this invention is more than -0.1V in the water solution with which natural electrode potential (saturated calomel electrode for S C E) contains 10 ppm of Cu ion, and is having formed in the maximum surface on the front face of a magnet nickel plating coat which has a property beyond 0V in the water solution containing 100 ppm of Cu ion, and demonstrates the corrosion resistance which was excellent even if it immersed and used it for the corrosive high electrolytic solution (etching fluid) by the oxidizing quality. There is a method of making nickel plating coat contain S which makes an aromatic series sulfonic acid or its salt a source of supply by performing electric nickel plating using nickel plating liquid containing an aromatic series sulfonic acid or its salt, for example as the manufacture approach of the subaqueous use mold rare earth system permanent magnet of this invention.

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最終頁に続く

(54) 【発明の名称】 水中使用型希土類系永久磁石およびその製造方法

(57) 【要約】

【課題】 酸化性で腐食性の高い電解質溶液（腐食液）に浸漬して使用しても優れた耐食性を発揮する水中使用型希土類系永久磁石およびその製造方法を提供すること。

【解決手段】 自然電極電位（対SCE飽和カロメル電極）がCuイオンを10ppm含む水溶液中で-0.1V以上であり、かつ、Cuイオンを100ppm含む水溶液中で0V以上の特性を有するNiめっき被膜を磁石表面の最表層に形成したことを特徴とする。

【特許請求の範囲】

【請求項1】 自然電極電位（対SCE飽和カロメル電極）がCuイオンを10ppm含む水溶液中で-0.1V以上であり、かつ、Cuイオンを100ppm含む水溶液中で0V以上の特性を有するNiめっき被膜を磁石表面の最表層に形成したことを特徴とする水中使用型希土類系永久磁石。

【請求項2】 前記Niめっき被膜が芳香族スルホン酸またはその塩を供給源とするSを含有することを特徴とする請求項1記載の水中使用型希土類系永久磁石。

【請求項3】 前記Niめっき被膜のS含有量が10ppm～800ppmであることを特徴とする請求項2記載の水中使用型希土類系永久磁石。

【請求項4】 前記Niめっき被膜の平均電析結晶粒径が0.1μm以下であることを特徴とする請求項1乃至3のいずれかに記載の水中使用型希土類系永久磁石。

【請求項5】 磁石表面に多層めっき被膜層を形成するに際しての最表層としての前記Niめっき被膜の膜厚が0.1μm～10μmであることを特徴とする請求項1乃至4のいずれかに記載の水中使用型希土類系永久磁石。

【請求項6】 前記Niめっき被膜が下層となるNiめっき被膜の表面に形成されていることを特徴とする請求項5記載の水中使用型希土類系永久磁石。

【請求項7】 希土類系永久磁石がR-Fe-B系永久磁石であることを特徴とする請求項1乃至6のいずれかに記載の水中使用型希土類系永久磁石。

【請求項8】 芳香族スルホン酸またはその塩を含有するNiめっき液を使用して電気Niめっきを行うことにより、自然電極電位（対SCE飽和カロメル電極）がCuイオンを10ppm含む水溶液中で-0.1V以上であり、かつ、Cuイオンを100ppm含む水溶液中で0V以上の特性を有するNiめっき被膜を磁石表面の最表層に形成することを特徴とする水中使用型希土類系永久磁石の製造方法。

【請求項9】 希土類系永久磁石表面の最表層に形成されるNiめっき被膜の水溶液中における自然電極電位がCuイオンとCuの平衡電位（ Cu^{2+}/Cu 平衡電位）以上となるように、Niめっき液中に芳香族スルホン酸またはその塩を含有させることを特徴とする芳香族スルホン酸またはその塩の希土類系永久磁石を製造するための使用方法。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】本発明は、酸化性で腐食性の高い電解質溶液（腐食液）に浸漬して使用しても優れた耐食性を発揮する水中使用型希土類系永久磁石およびその製造方法に関する。

【0002】

【従来の技術】Nd-Fe-B系永久磁石に代表される

R-Fe-B系永久磁石などの希土類系永久磁石は、高い磁気特性を有しているが、酸化腐食されやすい金属種（特にR）を含むので、表面処理を行わずに使用した場合には、わずかな酸やアルカリや水分などの影響によって表面から腐食が進行して錆が発生し、それに伴って、磁気特性の劣化やばらつきを招くことになる。さらに、磁気回路などの装置に組み込んだ磁石に錆が発生した場合、錆が飛散して周辺部品を汚染する恐れがある。従って、これらの問題点を回避するために、従来から、該磁石に要求される耐食性を付与すべく電気Niめっきにより、耐食性被膜としてのNiめっき被膜をその表面に形成することが行われている。

【0003】

【発明が解決しようとする課題】ところで、井戸水汲み上げ用や送液用の水中ポンプ、家電送液ポンプ、自動車の熱交換器部品用のモーターなどに使用される磁石としては、耐食性に優れたフェライト磁石が従来から使用されてきているが、ポンプやモーターなどの小型化による省スペース化や効率アップによる省エネルギー化などの要請から高い磁気特性を有する希土類系永久磁石をフェライト磁石に代えて使用することが検討されている。しかしながら、希土類系永久磁石を水中で使用されるこれらの用途に供するためには当然のことながら大気中で使用されるものよりも優れた耐食性が要求される。特に家電や自動車などのエアコンエバポレーター、コンデンサ、ラジエーター、暖房ヒーターなどの熱交換器部品用のモーターにおいては、液循環系の構成材料、大気環境、補給液などから不可避免的に混入するCuイオン、塩素イオン（塩分）、硫酸イオン、硝酸イオン、炭酸イオンなどの不純物イオンや溶存酸素などの影響により、磁石が使用される環境が酸化性で腐食性の高い電解質溶液（腐食液）環境となる場合がある。不純物イオンの中でもCuイオンや塩素イオンは腐食性が高く、とりわけ、Cuイオンは強酸化性であるため、希土類系永久磁石表面にNiめっき被膜を形成した場合でも、CuイオンがNiめっき被膜表面に置換析出して腐食の起点になったり、局部電池を形成して深さ方向の腐食を進行させる傾向が強く、結果的に、磁石素地に至る腐食（孔食や点食）により磁気特性が大きく劣化してしまうなどの使用上の問題がある。従って、希土類系永久磁石を水中で使用する場合にはCuイオンや塩素イオンに対して如何にして耐食性を向上させるかが重要な課題となる。そこで本発明は、酸化性で腐食性の高い電解質溶液（腐食液）に浸漬して使用しても優れた耐食性を発揮する水中使用型希土類系永久磁石およびその製造方法を提供することを目的とする。

【0004】

【課題を解決するための手段】本発明者らは、上記の点に鑑み種々の検討を行う過程において、水溶液中におけるCuイオンとCuの平衡電位（ Cu^{2+}/Cu 平衡電

位)に着目し、自然電極電位が該平衡電位以上という特性を有するNiめっき被膜を希土類系永久磁石表面の最表層に形成することにより、酸化性で腐食性の高い電解質溶液(腐食液)に浸漬して使用しても優れた耐食性を発揮する磁石が得られることを知見した。

【0005】本発明は、上記の知見に基づいてなされたものであり、本発明の水中使用型希土類系永久磁石は、請求項1記載の通り、自然電極電位(対SCE飽和カロメル電極)がCuイオンを10ppm含む水溶液中で-0.1V以上であり、かつ、Cuイオンを100ppm含む水溶液中で0V以上の特性を有するNiめっき被膜を磁石表面の最表層に形成したことを特徴とする。また、請求項2記載の水中使用型希土類系永久磁石は、請求項1記載の水中使用型希土類系永久磁石において、前記Niめっき被膜が芳香族スルホン酸またはその塩を供給源とするSを含有することを特徴とする。また、請求項3記載の水中使用型希土類系永久磁石は、請求項2記載の水中使用型希土類系永久磁石において、前記Niめっき被膜のS含有量が10ppm~800ppmであることを特徴とする。また、請求項4記載の水中使用型希土類系永久磁石は、請求項1乃至3のいずれかに記載の水中使用型希土類系永久磁石において、前記Niめっき被膜の平均電析結晶粒径が0.1μm以下であることを特徴とする。また、請求項5記載の水中使用型希土類系永久磁石は、請求項1乃至4のいずれかに記載の水中使用型希土類系永久磁石において、磁石表面に多層めっき被膜層を形成するに際しての最表層としての前記Niめっき被膜の膜厚が0.1μm~10μmであることを特徴とする。また、請求項6記載の水中使用型希土類系永久磁石は、請求項5記載の水中使用型希土類系永久磁石において、前記Niめっき被膜が下層となるNiめっき被膜の表面に形成されていることを特徴とする。また、請求項7記載の水中使用型希土類系永久磁石は、請求項1乃至6のいずれかに記載の水中使用型希土類系永久磁石において、希土類系永久磁石がR-Fe-B系永久磁石であることを特徴とする。また、本発明の水中使用型希土類系永久磁石の製造方法は、請求項8記載の通り、芳香族スルホン酸またはその塩を含有するNiめっき液を使用して電気Niめっきを行うことにより、自然電極電位(対SCE飽和カロメル電極)がCuイオンを10ppm含む水溶液中で-0.1V以上であり、かつ、Cuイオンを100ppm含む水溶液中で0V以上の特性を有するNiめっき被膜を磁石表面の最表層に設けることを特徴とする。また、本発明の芳香族スルホン酸またはその塩の希土類系永久磁石を製造するための使用方法は、請求項9記載の通り、希土類系永久磁石表面の最表層に形成されるNiめっき被膜の水溶液中における自然電極電位がCuイオンとCuの平衡電位(Cu^{2+}/Cu 平衡電位)以上となるように、Niめっき液中に芳香族スルホン酸またはその塩を含有させることを特徴とす

る。

【0006】

【発明の実施の形態】本発明の水中使用型希土類系永久磁石は、自然電極電位(対SCE飽和カロメル電極)がCuイオンを10ppm含む水溶液中で-0.1V以上であり、かつ、Cuイオンを100ppm含む水溶液中で0V以上の特性を有するNiめっき被膜を磁石表面の最表層に形成したことを特徴とするものである。希土類系永久磁石表面の最表層にこの特性を有するNiめっき被膜を形成することにより、該被膜の水溶液中における自然電極電位をCuイオンとCuの平衡電位(Cu^{2+}/Cu 平衡電位)以上とすることで、酸化性で腐食性の高い電解質溶液(腐食液)に浸漬して使用しても優れた耐食性を発揮する磁石とする。なお、より優れた耐食性を付与するためには自然電極電位(対SCE飽和カロメル電極)がCuイオンを10ppm含む水溶液中で0V以上であり、かつ、Cuイオンを100ppm含む水溶液中で0.1V以上の特性を有するNiめっき被膜を形成することが望ましい。

【0007】本発明において自然電極電位とは、水溶液中においてNiめっき被膜の表面で複数の化学反応が起きている際のNiと水溶液との間の電位を意味し、具体的には、アノード反応としてのNiの溶解反応($Ni \rightarrow Ni^{2+} + 2e^-$)、カソード反応としてのCuイオンの還元反応($Cu^{2+} + 2e^- \rightarrow Cu$ 、 $Cu^{2+} + e^- \rightarrow Cu^+$)や溶存酸素の還元反応($O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$)などに基づく混成電位を意味する。

【0008】自然電極電位(対SCE飽和カロメル電極)がCuイオンを10ppm含む水溶液中で-0.1V以上であり、かつ、Cuイオンを100ppm含む水溶液中で0V以上の特性を有するNiめっき被膜を希土類系永久磁石表面の最表層に形成する方法としては、例えば、芳香族スルホン酸またはその塩を含有するNiめっき液を使用して電気Niめっきを行うことにより、Niめっき被膜に芳香族スルホン酸またはその塩を供給源とするSを含有させる方法がある。

【0009】希土類系永久磁石の電気Niめっきにおいては、一般的にめっき浴(ワット浴など)組成単独では緻密で光沢性に優れたNiめっき被膜を形成することができないことから、従来からめっき被膜中にサッカリンに代表される芳香族スルホンイミドや芳香族スルホンアミドを供給源とするSを含有させてめっき被膜を緻密化させる方法が広く採用されている。しかしながら、このようにしてめっき被膜中にSを含有させると、Niめっき被膜の表面電位が下がるので、電気化学的にめっき被膜自身の耐食性が低下することになる。上記の現象を利用して、希土類系永久磁石表面に多層Niめっき被膜を形成するに際して、最表層のNiめっき被膜にのみSを含有させたり(例えば特開平2-23603号公報を参照)、磁石表面から上層のNiめっき被膜になるほどS

の含有量を多くして意図的に表面電位を下げる（例えば特開平4-267305号公報や特許第2941446号公報を参照）ことで上層のNiめっき被膜を優先的に腐食させるようにして全体としての耐食性を向上させる方法が提案されているが、Cuイオンなどを含む腐食液中でこのような磁石を使用した場合、磁石表面の最表層のNiめっき被膜の自然電極電位が Cu^{2+}/Cu 平衡電位よりも低くなってしまうことでCuイオンがNiめっき被膜表面に置換析出してしまい、その結果、腐食が進行して十分な耐食性を確保することができなかった。ところが、本発明者らの検討によって、Niめっき被膜中に含有させるSの供給源として、広く使用されている芳香族スルホンイミドや芳香族スルホンアミドを使用した場合、上記のような問題が起こるのにもかかわらず、芳香族スルホン酸またはその塩をSの供給源として使用した場合、Cuイオンなどを含む腐食液に浸漬して使用しても優れた耐食性を発揮するNiめっき被膜が形成されることが判明した。

【0010】ここで、芳香族スルホン酸としては、ベンゼンスルホン酸や1, 3, 6ナフタレントリスルホン酸などが挙げられる。芳香族スルホン酸の塩としては、ナトリウム塩やカリウム塩などが挙げられる。

【0011】Niめっき液への芳香族スルホン酸またはその塩の添加は、形成されるNiめっき被膜のS含有量が10ppm～800ppmとなるように行うことが望ましい。形成されるNiめっき被膜のS含有量が10ppmよりも少ないとその効果が十分に発揮されない恐れがあり、800ppmよりも多いと脆くて密着性に欠けるNiめっき被膜となる恐れがある。

【0012】芳香族スルホン酸またはその塩の添加対象となるNiめっき液は、特段限定されるものではなく、電気Niめっきに使用される自体公知のもの、例えば、ワット浴、スルファミン酸浴、塩化物浴、ほうふつ化物浴、塩化アンモニウム浴などに使用されるものでよい。電気Niめっき条件は個々のめっき浴に応じた自体公知の条件を設定して行えばよい。なお、必要に応じて、電気Niめっき後に熱処理（ベーキング）を大気中で150℃～250℃にて10分～1時間程度行ってもよい。この処理により、形成されるNiめっき被膜の水溶液中での自然電極電位をより貴な方向に移動させることがで

きる。

【0013】自然電極電位（対SCE飽和カロメル電極）がCuイオンを10ppm含む水溶液中で-0.1V以上であり、かつ、Cuイオンを100ppm含む水溶液中で0V以上の特性を有するNiめっき被膜は、被膜の緻密化の観点からその平均電析結晶粒径が0.1μm以下となるように形成することが望ましい。このようなめっき被膜は、Niめっき液に上記の芳香族スルホン酸またはその塩を単独で添加したり、これを例えばポリエチレングリコールなどのアルコール系添加剤と組み合

わせて添加することなどで形成することができる。なお、電析結晶粒径はFE-SEM（電界放射型走査顕微鏡）やAFM（原子間力顕微鏡）による観察によって測定することができる。

【0014】自然電極電位（対SCE飽和カロメル電極）がCuイオンを10ppm含む水溶液中で-0.1V以上であり、かつ、Cuイオンを100ppm含む水溶液中で0V以上の特性を有するNiめっき被膜の膜厚は、希土類系永久磁石表面にこのNiめっき被膜のみを形成する場合は5μm～30μmが望ましく、磁石表面に多層めっき被膜層を形成するに際しての最表層にこのNiめっき被膜を形成する場合は0.1μm～10μmが望ましい。磁石表面に多層めっき被膜層を形成するに際しての最表層にこのNiめっき被膜を形成する場合におけるその下層は、電気めっきや無電解めっきなどの湿式めっきや、気相めっきなど、自体公知の方法で形成されるNiめっき被膜をはじめとする種々の金属めっき被膜でよく、例えば、第1層が公知のNiめっき被膜で第2層（最表層）がこのNiめっき被膜、第1層と第2層が公知のNiめっき被膜で第3層（最表層）がこのNiめっき被膜、第1層が公知のNiめっき被膜で第2層が公知のCuめっき被膜で第3層（最表層）がこのNiめっき被膜などの形態がある。

【0015】本発明に適用される希土類系永久磁石の内、R-Fe-B系永久磁石における希土類元素（R）は、Nd、Pr、Dy、Ho、Tb、Smのうち少なくとも1種、あるいはさらに、La、Ce、Gd、Er、Eu、Tm、Yb、Lu、Yのうち少なくとも1種を含むものが望ましい。また、通常はRのうち1種をもって足りるが、実用上は2種以上の混合物（ミッシュメタルやジウムなど）を入手上の便宜などの理由によって使用することもできる。さらに、Al、Ti、V、Cr、Mn、Bi、Nb、Ta、Mo、W、Sb、Ge、Sn、Zr、Ni、Si、Zn、Hf、Gaのうち少なくとも1種を添加することで、保磁力や減磁曲線の角型性の改善、製造性の改善、低価格化を図ることが可能となる。また、Feの一部をCoで置換することによって、得られる磁石の磁気特性を損なうことなしに温度特性を改善することができる。

【0016】

【実施例】本発明を以下の実施例によってさらに詳細に説明するが、本発明は以下の記載に何ら限定されるものではない。

【0017】粉末冶金法により作製した15Nd-1Dy-7B-77Fe（原子%）の組成をもつ焼結体をアルゴン雰囲気中600℃で2時間時効処理を施し、厚さ2mm、幅15mm、長さ30mmの平板状に加工し、さらにバレル面取り加工を行って得られた焼結磁石を希釈硝酸で酸洗洗浄した。水洗後にさらにアルカリ液で電解洗浄し、水洗した。この磁石に対し、硫酸ニッケル

・6水和物260g/l、塩化ニッケル・6水和物40g/l、ホウ酸40g/l、添加剤としてプロパギアルコールを0.5g/lを含み、pHを4に調整したNiめっき液を使用し、めっき浴の液温50℃、電流密度0.2A/dm²、陽極としてNi板という電気Niめっき条件にて、膜厚が20μmのNiめっき被膜を第1層めっき被膜として磁石表面に形成した。次に、硫酸ニッケル・6水和物300g/l、塩化ニッケル・6水和物50g/l、ホウ酸30g/l、クエン酸ナトリウム10g/l、表1に示した各種の濃度に調整した添加剤を含み、pHを4に調整したNiめっき液を使用し、めっき浴の液温50℃、電流密度0.3A/dm²、陽極としてNi板という電気Niめっき条件にて、膜厚が5μmのNiめっき被膜を第2層（最表層）めっき被膜として第1層めっき被膜表面に形成した。第2層Niめっき被膜について、EPMA（電子線マイクロアナライザー：島津製作所社製EPM-810を使用）を使用して測定したS含有量と、AFM（原子間力顕微鏡：島津製作所社製SPM-9500を使用）を使用して測定した平均電析結晶粒径を表1に示す。上記のようにして得られためっき磁石サンプルを水洗して乾燥させた後、これをCuイオン100ppm（塩化銅・2水和物で調整）と塩素イオン200ppm（塩化ナトリウムで調整）を含有してさらに溶存酸素が存在する50℃の腐食液1と、Cuイオン10ppm（同）と塩素イオン200ppm（同）を含有してさらに溶存酸素が存在する50℃の腐食液2（いずれの腐食液もpHは6.5～7）に浸漬し第2層Niめっき被膜の自然電極電位を測定するとともにその性能を評価した。結果を表1に示す。

【0018】表1において、自然電極電位の測定は以下* 30

* のようにして行った。即ち、500mlビーカーに腐食液を入れ液温50℃とした。めっき磁石サンプルを腐食液に浸漬してから30分経過後、一般的な飽和塩化カリウム溶液を寒天詰めしたガラス製ルギン管を用い、参照電極をSCE飽和カロメル電極としてサンプル表面の電位を市販のポテンシostat装置により測定することにより行った（自然電極電位の測定はNiめっき被膜表面の電位が安定する腐食液浸漬20分～30分経過後に行うことが望ましい）。なお、この測定はビーカー内をマグネットスターラーにて500rpmで攪拌しながら行った。

【0019】表1における被膜健全性の評価はめっき被膜の緻密性及び耐食性促進評価（発色反応試験）により行った。評価方法を簡単に説明すると以下の通りである。フェリシアン化カリウム3g/l、エタノール100ml/lおよび塩酸にてpH2に調整した試験液にめっき磁石サンプルを常温で浸漬して60分間観察した。磁石素材に腐食が至ったり被膜欠陥（ピンホールなど）が存在する場合には青色斑点が発生するので、60分浸漬後も青色斑点の発生がない場合は○、浸漬後30分以上で青色斑点が発生した場合は△、浸漬後10分～20分で青色斑点が発生した場合は×と評価した。

【0020】表1における耐食性の評価はめっき磁石サンプルを液温50℃の腐食液1に1000時間浸漬し、赤錆の発生と着磁後のフラックス量測定に基づく磁気特性劣化を調べ、赤錆発生がなく、かつ、減磁率が1%以下の場合は○、それ以外の場合は×と評価することで行った。

【0021】

【表1】

Niめっき液添加剤		添加量 (g/l)	S含量 (ppm)	平均電析 結晶粒径 (μm)	自然電極電位 浸漬30分後のmV vs SCE		被膜 健全性	耐食性	備考
					腐食液1				
					Cu ²⁺ :100ppm	Cu ²⁺ :10ppm			
1	1,3,6ナフトレントリスルホン酸ナトリウム	0.8	200	<0.1	+220	+160	○	○	本発明例
2	ベンゼンスルホン酸	1	250	<0.1	+150	+90	○	○	本発明例
3	1,3,6ナフトレントリスルホン酸ナトリウム +アリルスルホン酸	2+0.5	300	<0.1	+220	+150	○	○	本発明例
4	1,3,6ナフトレントリスルホン酸ナトリウム +ナリエチレングリコール分子量1000	5+0.05	700	<0.1	+170	+120	○	○	本発明例
5	チオ尿素+プロパギルアルコール	1+0.5	≦20	<0.1	+230	+180	○	○	本発明例
6	ナリエチレングリコール分子量3000	0.03	≦20	<0.1	+180	+150	○	○	本発明例
7	サッカリン	5	800	<0.1	-50	-100	×	×	比較例
8	サッカリン+2ブチン1,4ジオール	3+0.5	500	<0.1	-10	-70	△	×	比較例
9	パラトルエンスルホンアミド	10	1200	<0.1	-30	-150	×	×	比較例

【0022】表1から明らかなように、芳香族スルホン酸やその塩を含有するNiめっき液を使用して電気Niめっきを行うことにより、自然電極電位（対SCE飽和

カロメル電極）がCuイオンを10ppm含む水溶液中で-0.1V以上であり、かつ、Cuイオンを100ppm含む水溶液中で0V以上の特性を有し、腐食液に浸

漬して使用しても優れた耐食性を発揮するNiめっき被膜を形成することができることがわかった。一方、芳香族スルホンイミドや芳香族スルホンアミドを含有するNiめっき液を使用して電気Niめっきを行った場合、形成されるNiめっき被膜は、そのS含有量が芳香族スルホン酸やその塩を含有するNiめっき液を使用して電気Niめっきを行うことにより形成されるNiめっき被膜のS含有量と同程度であっても、水溶液中での自然電極電位が大きく低下して卑となり、腐食液に浸漬して使用した場合、耐食性を維持できないことがわかった。この違いは、芳香族スルホン酸やその塩をSの供給源として使用した場合と芳香族スルホンイミドや芳香族スルホンアミドをSの供給源として使用した場合との間での、形成されるNiめっき被膜中でのSの供給源としてのこれらの添加剤の析出状態の違いや、Niめっき被膜中のSの分布の均一性の差に基づくものであると推察される。また、チオ尿素とプロパギルアルコールを組み合わせ*

* Niめっき液に添加した場合やポリエチレングリコールをNiめっき液に添加した場合にも芳香族スルホン酸やその塩と同様の効果が得られることがわかった。

【0023】

【発明の効果】本発明の水中使用型希土類系永久磁石は、自然電極電位（対SCE飽和カロメル電極）がCuイオンを10ppm含む水溶液中で-0.1V以上であり、かつ、Cuイオンを100ppm含む水溶液中で0V以上の特性を有するNiめっき被膜を磁石表面の最表層に形成したことで、酸化性で腐食性の高い電解質溶液（腐食液）に浸漬して使用しても優れた耐食性を発揮する。本発明の水中使用型希土類系永久磁石の製造方法としては、例えば、芳香族スルホン酸またはその塩を含有するNiめっき液を使用して電気Niめっきを行うことにより、Niめっき被膜に芳香族スルホン酸またはその塩を供給源とするSを含有させる方法がある。

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